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ENVIRONMENTAL DURABILITY OF FIBER REINFORCED COMPOSITES

FINAL REPORT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
An investigation has been completed which determines the physiochemical mechanisms of environmental durability and degradation of graphite-epoxy (Thornel T300 in 5208 epoxy) and fiber glass-epoxy S-2 glass in 5208 epoxy) under hydro-thermal (high moisture and temperature) exposure. Surface energy and moisture diffusion analysis provide nondestructive test methods which detect irreversible degradation of the fiber-matrix interface. Dynamic mechanical damping detects reversible volumetric plasticization effect on modulus, and the interlaminar shear strength and transfibrous fracture energy

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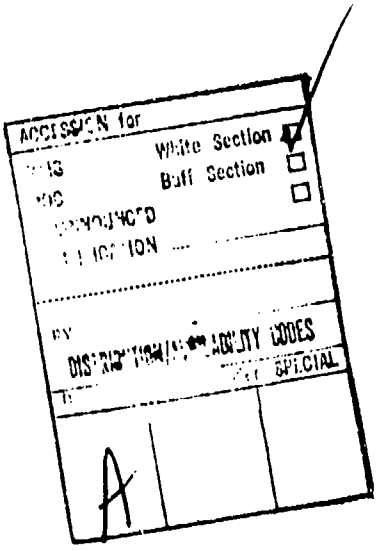
distributions. A composite durability characterization program is demonstrated which effectively combines preventative nondestructive evaluation (PNDE) with environmental failure and micromechanics analysis of composite structural reliability.

PREFACE

This final report summarizes the results of a detailed mechanistic study of environmental durability and degradation of fiber reinforced composites conducted under Army Research Office Contract No. DAAG29-77-C-0005, Project 1L161002 BH57-04. A comparative study of graphite (Union Carbide T300) and glass (Owens Corning S-2) uniaxial fiber reinforcements in a common epoxy matrix (NARMCO 5208) elucidates the discrete role of the fiber-matrix interfacial bond in controlling composite response to accelerated aging under combined high moisture and temperature cycling. This report outlines the technical approach and summarizes the significant results of this study.



INTRODUCTION

The major objective of this program is to determine the physio-chemical mechanisms of environmental durability and degradation of fiber reinforced epoxy composites under hydrothermal exposure (to combined high moisture and temperature). Parameters and mechanisms to be studied include interfacial chemistry and bonding between fiber and matrix as well as the effects of hydrothermal aging upon the bulk properties of the matrix and reinforced composite. In order to achieve a detailed separation of surface and interfacial mechanisms from environmental aging on matrix or fiber bulk properties, the three part outline shown in Table 1 was developed and applied in this study. Full details of test methods and analysis have been published in prior reports.[1-4]

The outline for composite durability characterization shown in Part 1 of Table 1 describes the procedure for analysis of separated fiber and uncured matrix. The results from this phase of the study are briefly summarized in Table 2 and Sections 1-4.

Part 2 of Table 1 details the combined nondestructive and destructive test program for the uniaxial reinforced composite subject to hydrothermal aging. The results of this phase of the study are summarized in Table 2, Sections 5-9.

Part 3 of Table 1 outlines the essential elements of data analysis and implementation of nondestructive testing (NDT) which permits composite durability assessment and defines improved matrix and interface chemistries.

SIGNIFICANT RESULTS

For convenience, the following paragraphs are numbered to coincide with the data summary of Table 2, Sections 1-9.

1. General Properties

Production lots of composite prepreg and standard production curing processes for the uniaxial reinforced laminates were employed to obtain a state-of-the-art composite for these studies. The cured laminates of 5208/T300 and 5208/S2 showed nearly equivalent fiber volume fraction and low void volume fraction.

2. Surface Energies

The surface energies of both uncured and cured epoxy from the 5208-T300 prepreg show dispersion (γ^d) and polar (γ^p) components of surface energy typical of other 350°F (177°C) surface ceiling composites. The T300 graphite fiber shows a high γ^p indicative of oxidative surface treatment.

The surface energies of the cured epoxy from 5208/S2 composites show values of γ^p higher than typical for epoxy which suggests surface migration of marginally soluble silane adhesion promoted from the bulk matrix during cure. The γ^d and γ^p for cured matrix and reactive silane coated glass fiber are shown in Table 2 as nearly equivalent.

3. Matrix Curing Kinetics

Both the exothermic heat of cure ΔH_p and the temperature T* of maximum reaction rate are shown to be slightly higher for the epoxy matrix of the 5208/T300 prepreg. The temperature dependence of cure rate as measured by the activation energy of cure E* is equivalent for the two prepregs. Both cure kinetics and infrared spectroscopic analysis indicate substantial equivalence of the 5208 epoxy in both graphite and glass laminates.

4. Cured Matrix Moisture Absorption at 75°C

Both the maximum moisture uptake (wt %) and diffusion coefficient of 5208 epoxy in this study are typical of literature values for this cured resin.

5. Dynamical Mechanical Damping of the Cured Composite

Thermal scans (rheovibron) for flexural damping maxima of the unaged uniaxial composite through the alpha (or glass) transition show substantial equivalence in magnitude of mechanical loss tangent maxima $\tan\delta_{max}$ of both 5208/T300 and 5208/S2 composite. Both composites display the high temperature and narrow temperature range for the alpha transition indicative of full cure and regular network structure.

Rheovibron dynamic scans of fully hydrated and redried composites showed the dominant water plasticizing effect which broadens the low temperature branch of the alpha transition. The redried composite shows a substantial reversibility to unaged damping response.

6. 75°C H_2O Absorption of Cured Composite

Using newly developed NDT studies for orthogonal moisture diffusion (see Ref. 3), the cumulative damage effects of three cycles of full hydration and drying are shown to produce a two to four-fold increase in diffusion coefficients D_2 and D_3 transverse to the fibers. Diffusion of moisture parallel to the fiber axis (D_1) is selectively increased over ten-fold in the 5208/S2 composite, clearly indicating a special mechanism of interface degradation not shown by the 5208/T300 laminate.

7. Transfibrous Composite Ultrasonic Response

Measurements of both ultrasonic wave velocity and apparent acoustic attenuation perpendicular to the fiber axis on unaged, fully

hydrated and redried specimens shows a reversible ultrasonic response as is also shown by low frequency (Rheovibron) measurements by thermal scan.

8. Interlamiar Shear Strength Distributions

Analysis of the interlaminar shear strength distributions for unaged, fully hydrated, and redried composites by Weibull (extreme value) statistics (see Ref. 3) shows higher average strength λ_o and lower strength degradation for 5208/T300 composite. This result agrees with predictions from surface energy and moisture diffusion analysis discussed above.

9. Transfibrous Fracture Energy Distributions

This study shows the expected result (see Ref. 4) that the high modulus T300 fiber (tensile modulus = $2.61 \cdot 10^6 Kg/cm^2$, e_b = 0.9%) produces lower average fracture energy, W_{Fo}, than the low modulus and more extensible S2 glass (tensile modulus = $9.2 \cdot 10^5 Kg/cm^2$, ε_b = 3.0%). The fracture energy distributions for 5108/T300 composite are shown to display significantly higher Weibull shape parameters m>10 indicative of well-defined fracture energy properties and low moisture degradation effects. Conversely, the 5208/S3 composite displays a lower Weibull parameter in m>3.0 and high energy degradation under moisture exposure. These results correlate with other PNDE measurements and show that the lower Weibull parameter m and higher moisture sensitivity of average energy, W_{Fo} for 5208/S2 composite greatly reduces the maximum safe design value of fracture energy, W_F, under constraints of high survival probability S>0.999. For example, using minimum values (see Table 2) of m = 10.8 and W_{Fo} = 65.4Kg/cm at survival probability S = 0.999 yields a design fracture energy W_F = 32.8Kg/cm for 5208/T300 while m = 2.83 and W_{Fo} = 213Kg/cm yields a 44% lower design fracture energy W_F = 18.5Kg/cm for 5208/S2 composite.

CONCLUSIONS

The results of this study and the data summary of Table 2 permit the following conclusions:

1. The higher moisture sensitivity for the epoxy/glass interface predicted by surface energy analysis of separated fiber and matrix, and moisture diffusion analysis of laminates is confirmed in both shear strength and fracture energy distributions.

2. Since surface energy analysis can be applied to both matrix and fiber prior to prepreg formation, these data can play an important role in preventive nondestructive evaluation (PNDE) for both materials selection, and control of surface treatment for interfacial bonding.

3. Moisture diffusion analysis is shown to be highly sensitive to irreversible hydrothermal aging effects in both epoxy/glass and epoxy/graphite composites, and to specifically indicate high epoxy/glass interface degradation.

4. Ultrasonic and low frequency (rheovibron) dynamic mechanical analysis detect the temporary water plasticizing effects, but fail to detect the non-volumetric irreversible degradation of internal interface integrity which is sensed by both surface energetics and moisture diffusion analysis.

5. The statistical analysis of both interlaminar shear strengths and transfibrous fracture energies provides structural integrity information which clearly illuminates critical design aspects of both environmental durability and environmental degradation.

6. The outline for composite durability characterization (see Table 1) which provides the results in Table 2 operates on small quantities of material (less than 6.0 cc prepreg and less than 250 cc cured uniaxial laminate).

7. When the systematic composite durability characterization of Table 1 is applied early in a composite development program, it follows that critical materials and design data relevant to preventive nondestructive evaluation (PNDE) can be acquired and implemented in the primary composite design.

REFERENCES

1. D.H. Kaelble, P.J. Dynes, L.W. Crane and L. Maus, "Kinetics of Environmental Degradation in Graphite Epoxy Laminates," ASTM Special Technical Publication, STP 580 (1975), pp. 247-262.

2. D.H. Kaelble and P.J. Dynes, "Nondestructive Tests for Shear Strength Degradation of a Graphite-Epoxy Composite, ASTM Special Technical Publication, STP 617 (1977), pp. 190-200.

3. D.H. Kaelble and P.J. Dynes, "Methods for Detecting Moisture Degradation in Graphite-Epoxy Composites," Materials Evaluation Research Supplement, 35 (4) (April 1977), pp. 103-108.

4. D.H. Kaelble, "Theory and Analysis of Fracture Energy in Fiber Reinforced Composites," J. Adhesion 5, 245-264 (1973).

TABLE 1: Outline for Composite Durability Characterization

Part 1: Analysis of Separated Fiber and Matrix

- 1a. Obtain and separate uncured prepreg components
- 1b. Analyze fiber and matrix surface energies
- 1c. Analyze resin chemistry and curing mechanism
- 1d. Define curing kinetics and network structure
- 1e. Analyze hydrothermal aging effects on network structure.

Part 2: Analysis of Composite Laminate Aging

- 2a. Obtain composite laminates for aging studies
- 2b. Measure kinetics of water diffusion into composite
- 2c. Determine interlaminar shear strength versus moisture content.
- 2d. Determine fracture energy versus moisture content
- 2e. Measure dynamic mechanical (NDT) response versus moisture content.

Part 3: Data Analysis and NDT Methodology

- 3a. Determine relation between strength degradation mechanisms and NDT methodology.
- 3b. Design NDT experiments and statistical analysis for tracking strength degradation
- 3c. Define improved matrix and interface chemistries.

Table 2: Results of Environmental Durability Characterization of Epoxy/Graphite and Epoxy/Glass S-2 Composites with 150°C (350°F) Service Ceiling Temperature (Standard Cure, Uniaxial Reinforcement).

1. General Properties		System 1	System 2
Epoxy matrix		NARMCO 5208	NARMCO 5208
Fiber		Union Carbide Thornel T300 Graphite	Owens/Corning S-2 Glass
Fiber Finish		1% by fiber wt bisphenol-A epoxy	Reactive amino silane coupling agent (specified as A1100)
Post cure cycle		6 hr at 180°C	Standard
Fiber volume fraction		0.60	0.58
Void volume fraction		<0.01	<0.01
2. Surface Energies (dyn/cm) at 22°C			
Uncured matrix	γ^d	29.2 ± 2.3	29.0 ± 2.8
	γ^p	13.4 ± 2.8	17.8 ± 4.6
Cured matrix	γ^d	28.5 ± 2.1	25.3 ± 3.0
	γ^p	13.2 ± 2.3	32.8 ± 6.1
Fiber	γ^d	24.9 ± 2.6	23.5 ± 2.5
	γ^p	25.2 ± 3.8	30.7 ± 4.1

TABLE 2 (Cont'd)

3. Matrix Curing Kinetics by DSC	System 1		System 2	
Scan Rate (°C/min)	ΔH_D (cal/gm)	T* (°C)	ΔH_D (cal/gm)	T* (°C)
5	127	236	111	221
10	147	253	129	240
20	140	271	130	257
Cure activation energy (kcal/mole)	21		21	

4. Cured Matrix Moisture Absorption (at 75°C)	System 1	System 2
Max. H_2O uptake (wt%)	5.84	
Diffusion coefficient D_R (10^{-8} cm^2/sec)	1.45	

5. Dynamic Mechanical Damping of Cured Composite (110 Hz Flexure, Unaged		
Alpha $\tan\delta_{max}$	.12	.11
$\tan\delta_{max}$ temp (°C)	282	292
1/2 $\tan\delta_{max}$ temp range (°C)	24	32

TABLE 2 (Cont'd)

6. 75°C H_2O Absorption of Cured Composite Diffusion Coefficient ($D_1 = 10^{-6}$ cm^2/s)

Transfibrous surface (D_1)	1st cycle	0.76	0.94
	2nd	1.90	3.96
	3rd	2.11	10.40
Translaminar surface (D_2)	1st cycle	0.38	0.22
	2nd	1.17	0.72
	3rd	1.17	0.75
Interlaminar surface (D_3)	1st cycle	0.47	0.21
	2nd	0.74	0.62
	3rd	1.01	0.72

7. Transfibrous Composite Ultrasonic Response 23°C 2.25 MHz, Long Wave

	System 1	System 2
Attenuation (neper/cm)		
Unaged, dry	5.37	5.22
Aged, redried	5.17	5.31
Wave Velocity (km/s)		
Unaged, dry	3.13	
Aged, redried	3.13	

8. Interlaminar Shear Strength Distributions $S = \exp-(\lambda/\lambda_o)^m$

(Tests at 23°C)

	m	λ_o Kg/cm^2	m	λ_o Kg/cm^2
Unaged, dry	5.56	772	7.90	672
Aged, wet	5.59	679	5.88	493
Aged, redried	7.89	757	7.18	658

9. Transfibrous Fracture Energy Distributions $S = \exp-(W_F/W_{Fo})^m$

(Tests at 23°C)

	m	W_{Fo} (Kg/cm)	m	W_{Fo} (Kg/cm)
Unaged, dry	10.8	65.4	4.37	1212
Aged, wet	17.0	68.7	2.83	213
Aged, redried	14.1	75.9	4.23	459

LIST OF PUBLICATIONS AND PRESENTATIONS

The following were published or presented during the course of this program. The analysis of results described in this report is not yet complete and additional published work is anticipated.

1. P.J. Dynes and D.H. Kaelble, "Physiochemical Analysis of Graphite Epoxy Composite Systems," Proc. 5th Annual ASTM Conf. on Composite Materials: Testing and Design, New Orleans, March 1978.

2. D.H. Kaelble, "Environmental Durability of Fiber Reinforced Composites," ARO and AMMRC Workshop on the Effects of Environment on Polymer Matrix Composites," May 3, 1978, Watertown, Mass.

3. R.M. Panos, R.P. Haak, P.J. Dynes and D.H. Kaelble, "Experimental Analysis of Hydrothermal Aging in Fiber Reinforced Epoxies," to be presented at the ACS National Meeting, April 1-6, 1979, Honolulu, Hawaii.

4. D.H. Kaelble, "Environmental Durability of Fiber Reinforced Composites," Second Annual Army Composite Materials Research Review, co-sponsored by AMMRE and ARD, May 1-4, 1979, University of Massachusetts, Amherst, Ma.

5. R.M. Panos and P.J. Dynes, "Effect of Absorbed Water on the Fracture Energy of Fiber-Reinforced Epoxy," in preparation for J. Mater. Sci.

6. R.M. Panos, P.J. Dynes and R.P. Haak, "Orthogonal Diffusion of Water in Fiber Reinforced Epoxies," in preparation for J. Composite Materials.

LIST OF PARTICIPANTS

The following people participated at some time during the course of this program.

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P.J. Dynes:	Senior Staff Associate
R.P. Haak:	Staff Associate
R.M. Panos:	Member Technical Staff